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(54) Apparatus for X-ray studies of crystalline matter

(57) The apparatus for X-ray studies of crystalline matter comprises a horizontally extending base (1) supporting a movable stage (2). The stage (2) carries an X-ray source (5) and a detector (6) of diffracted X-rays, which is operationally connected with mechanisms (7, 8) for their independent relative and joint rotation about an axis parallel to the base (1). A bracket (11) mounted on the base (1) supports a mechanism (10) operatively connected to the sample holder (9) for its rotation about an axis parallel to the base (1). The sample holder (9), the mechanism (10), and the bracket (11) are disposed on one side of the axis of rotation of the stage (2).

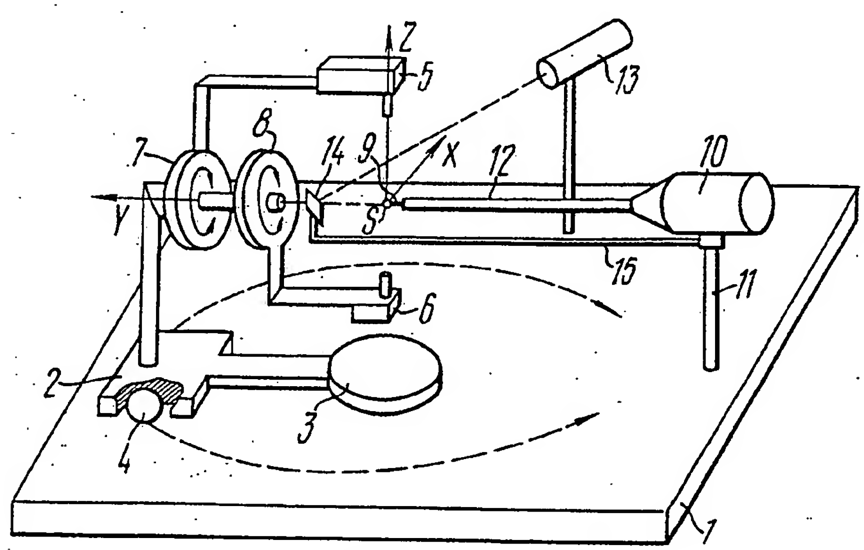

FIG. 1

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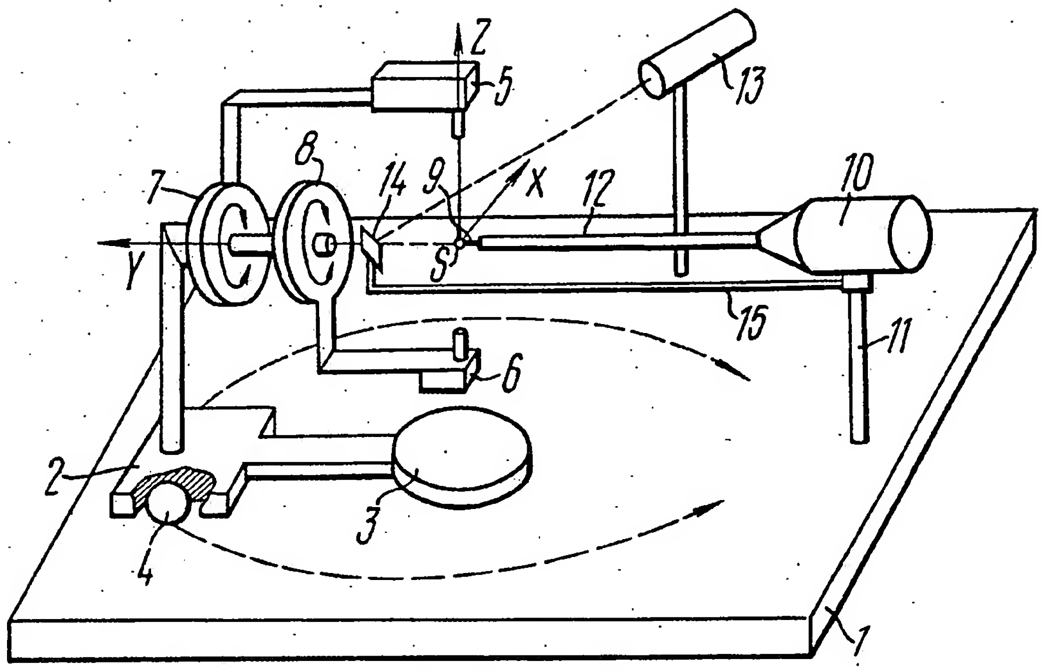
Z
5
13
8
7
14
9
X
12
10
Y
S
15
11
6
2
3
4
1

FIG. 1

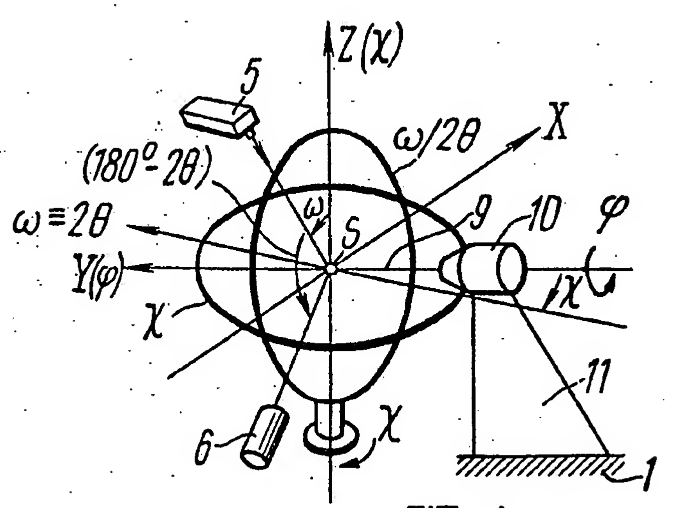
Z(χ)
5
ω/2θ
X
(180°-2θ)
ω≡2θ
ω
S
9
10
φ
Y(φ)
χ
χ
11
6
χ
1

FIG. 4

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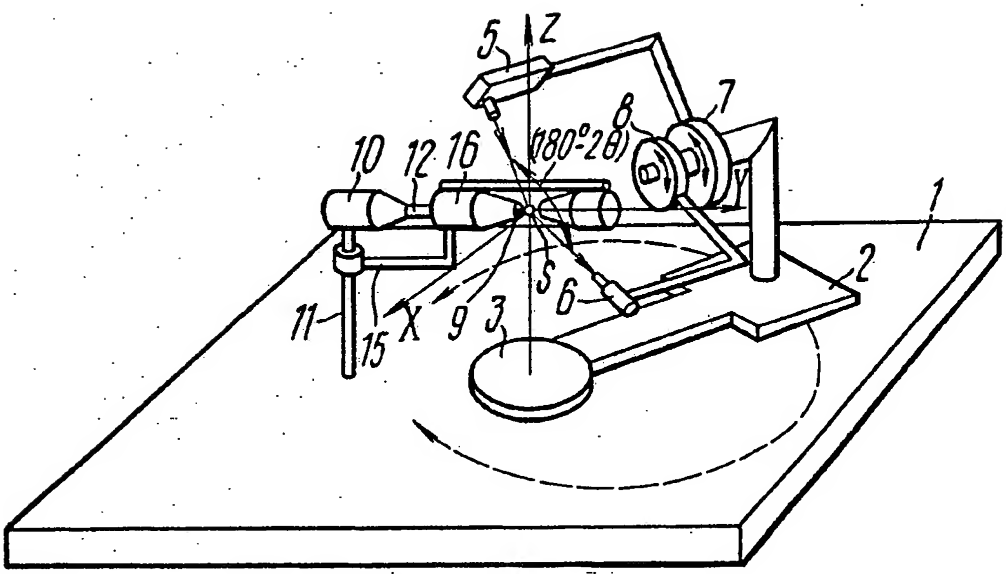

FIG. 2

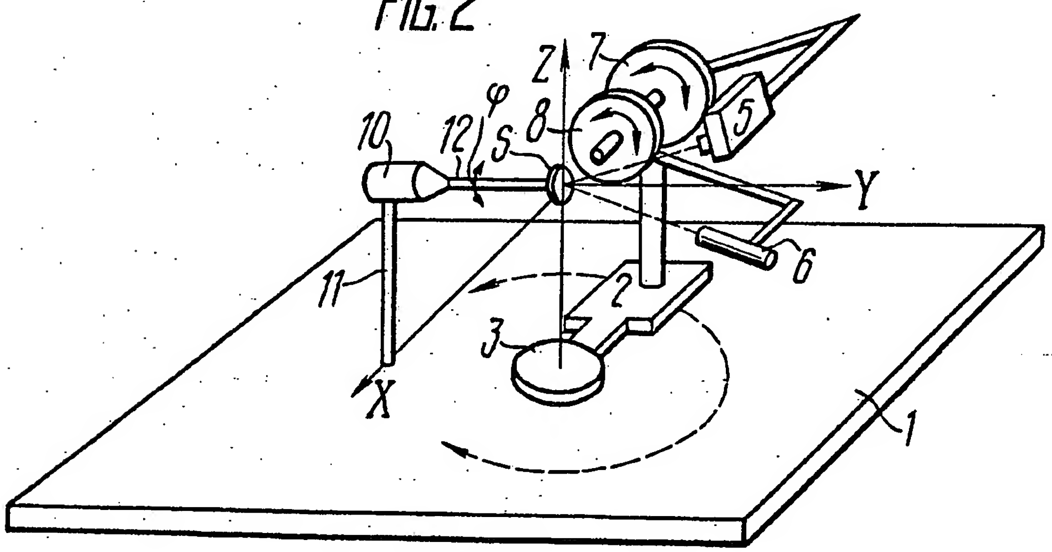

FIG. 3

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APPARATUS FOR X-RAY STUDIES OF CRYSTALLINE MATTER

The invention relates to investigation of materials with the use of diffracted radiation, and more particularly it relates to apparatus for X-ray studies of crystalline matter, mainly those operated for determining the integral intensities of reflection of X-rays by a single crystal under study with the aim of solving and refining its structure, for investigating electron density distribution in a single crystal, and also for measuring the intensity of radiation diffracted by a polycrystal for solving its structure, phase composition, texture, macro- and microdistortions of polycrystalline substances.

Finding solutions to such problems as changes of phases in fabrication of ferro-, piezo- and pyroelectrics, interaction of electromagnetic radiation, magnetic and electric fields with a substance is inherently related to solving and analyzing the structure of crystals. Investigation of processes taking place in crystals in their use and production in industries calls for an analysis of experimentally obtained data on the changes of their structure and electron distribution both in a normal environment and under the action of temperature, pressure, electromagnetic, magnetic and electric fields upon a sample. The most powerful among available tools for solving crystal structures and structures of molecules is X-ray structural analysis of single crystals. However, investigation of a structure under external action is complicated by the effect of the action upon a sample being

dependent on the direction of its application, and this direction should be maintained unchanged in the crystal while X-ray structural data are being obtained. Moreover, in the course of X-ray study of electron distributions in a crystal the gathering of reflections from the crystal should be as complete as possible, with losses in the areas of obscuration created by individual components of an apparatus for X-ray studies being kept at the minimum, and with every reflection, however weak, being registered.

There is known an apparatus commonly called a four-circle diffractometer with equatorial scanning geometry, comprising a source of X-rays, fixedly mounted on a horizontal base, a movable detector of X-radiation, a sample holder rotatable about its axis and fixedly secured on the movable ring of a circle made of two coaxial rings of which the outer one is mounted on a pivot aligned with the axis of rotation of the X-radiation detector. The axis of rotation of the detector is perpendicular to the direction of the primary beam of X-rays and to the axis of the circle made of the two coaxial rings. Their intersection point belongs to the axis of the sample holder, so that the sample is held at the intersection of all the said axes.

However, the abovedescribed design of a four-circle diffractometer would not allow for investigating crystal structures in an action upon the crystal under study in a steady predetermined crystallographic direction, e.g. of a direct beam of a laser or of a strong magnetic flux, as a direction most suitable for assessing the crystal, coinciding with the axis of rotation of the sample holder, may

attain any spatial position depending on the reflecting position of the crystal under study - from horizontal to vertical - so that is would be necessary to move the source of action upon the sample in synchronism with the motion of the sample holder, in order to maintain this action along the preset direction, which is manifestly impractical when the source of the action is a laser or the like. Furthermore, this design is prone to formation of "blind" or obscured areas in cryostatic studies, e.g. at the temperature of liquid helium.

There is further known an apparatus wherein the incorporation of the circle made of two coaxial rings has been replaced by rotation of the specimen holder about an additional axis inclined at 50° to the axis of rotation of the detector. However, this apparatus would neither provide for investigating the structure of crystals acted upon by electromagnetic, magnetic or physical forces.

The closest prior art of the present invention is the apparatus for X-ray studies of crystalline matter comprising a horizontally extending base supporting a movable stage operatively connected with a mechanism for its rotation about an axis perpendicular to the base and carrying a source of X-radiation and a detector of diffracted X-radiation, operatively connected with mechanisms for their independent relative and joint rotation about an axis parallel with the base, and a holder of a sample of crystalline matter operatively connected with a mechanism for its rotation about an axis parallel with the base, supported on the base with the aid of a bracket.

In the aobvedescribed apparatus for X-ray studies of

crystalline matter the bracket supporting the mechanism for rotating the sample holder on the base has an arcuate cantilever arm, with the spot of attachment of the bracket on the base and the mechanism for rotating the specimen holder being disposed to different sides of the axis of rotation of the stage. This arrangement impedes bringing the source and detector of X-rays closer to the sample under study, which, however, is essential in investigation of weakly reflecting crystals. Furthermore, this arrangement creates a substantial "blind zone" in the space at the side of the specimen holder, curtailing the number of reflections available for registration. The arcuate cantilever arm also produces an obscuration area.

This arrangement renders impossible registration of a diffraction pattern produced by flat polycrystalline samples rotated about a normal to their surface, which is a procedure normally associated with powder diffractometers; moreover, it limits the capacity for moving a sample or specimen under study from the point of intersection of the geometric axes of the stage and of the mechanisms for rotating the source and detector, for setting the focusing geometry in investigation of polycrystals.

Furthermore, the geometry of the apparatus of the prior art imposes strict limitations on the maximum dimensions of a source of action upon a specimen under study, e.g. a helium cryostat, high-power superconducting magnets and the like, thus all but prohibiting their employment for studies conducted on the apparatus.

It is an object of the present invention to create an apparatus for roentgenographic studies of crystalline matter,

providing for investigation of electron density distribution both in normally and weakly reflecting single crystals, as well as for solving the structure, phase composition, texture, macro- and microdistortions of polycrystals.

It is another object of the present invention to provide for implementing any required focusing geometry for studies of polycrystals.

With these and other objects in view, the present invention resides in an apparatus for X-ray studies of crystalline matter, comprising a horizontally extending base supporting a movable stage operatively connected with a mechanism for its rotation about an axis perpendicular to the base, the stage having mounted thereon a source of X-radiation and a detector of diffracted X-radiation, operatively connected with mechanisms for their independent relative and joint rotation about an axis parallel with the base, and a holder of a sample of crystalline matter operatively connected with a mechanism for its rotation about an axis parallel with the base, supported on the base with the aid of a bracket, in which apparatus, in accordance with the present invention, the holder of a sample of crystalline matter, the mechanism for its rotation about an axis parallel with the base and the bracket are disposed to one and the same side of the axis of rotation of the stage.

It is expedient that the apparatus for X-ray studies should also comprise an extension assembly connecting the holder of a sample of crystalline matter with the mechanism for its rotation about an axis parallel with the base.

It is also expedient that the apparatus for roentgenographic studies should comprise at least one source of

action upon the sample of crystalline matter for solving its structure and determining its electron density distribution in such action.

An apparatus for X-ray studies of crystalline matter, constructed in accordance with the invention, provides for investigating electron density distribution in single crystals, for solving the structure, phase composition, texture, macro- and microdistortions of polycrystals, while allowing for implementing any required focusing geometry for investigation of polycrystals.

The present invention will be further described in connection with its embodiments, with reference being made to the accompanying drawings, wherein:

FIG. 1 is a schematic perspective view of an apparatus for X-ray studies of crystalline matter, embodying the invention, incorporating a laser unit;

FIG. 2 is a modification of the apparatus embodying the invention, illustrated in FIG. 1, without a laser unit, but with a source of magnetic flux;

FIG. 3 is a modification of the apparatus embodying the invention, illustrated in FIG. 1, for investigation of polycrystalline substances in Bragg-Brentano focusing geometry, without a laser unit;

FIG. 4 schematically illustrates the attitudes of the geometric axes in the embodiment of the disclosed apparatus, illustrated in FIG. 2, showing the angles of rotation of the radiation source, radiation detector, sample holder and stage in a four-circle scanning geometry, in accordance with the invention.

The apparatus for X-ray studies of crystalline matter, constructed in accordance with the invention, comprises a horizontally extending base 1 (FIG. 1) supporting a movable stage 2 fixedly operatively connected with a mechanism 3 for its rotation about Z-axis perpendicular to the base 1. In the presently described embodiment the mechanism 3 for rotating the stage 2 includes an electric motor associated with a transmitter of the angle of rotation (not shown).

The stage 2 is mounted on the base 1 in the presently described embodiment for motion on three rolling-contact spherical bearings 4 uniformly spaced along a circle (only one such bearing 4 is shown in FIG. 1). The stage 2 has mounted thereon an X-radiation source 5 and a detector 6 of diffracted X-radiation, operatively connected with the respective mechanisms 7 and 8 for their relative independent and joint rotation about an axis parallel with the base 1. The mechanisms 7 and 8 are electric drives including angle--of-rotation transmitters (not shown in the drawings).

The apparatus further comprises a holder 9 of a sample of crystalline matter to be studied under normal conditions and under action upon it of electromagnetic, magnetic or electric fields, physical forces or temperature. The holder 9 is operatively connected with a mechanism 10 for its rotation about an axis parallel with the base 1 (Y-axis), supported on the base 1 with the aid of a bracket 11. The sample holder 9, the mechanism 10 for its rotation and the bracket 11 are disposed to one and the same side of the

Z-axis of rotation of the stage 2.

The apparatus for X-ray studies of crystalline matter further comprises an extension means 12 connected with the mechanism 10 for rotating the specimen holder 9 and with the specimen holder 9 itself. In the presently described embodiment the extension means is a simple rod, whereas in other embodiments the extension means may be of a telescopic design.

For investigating a specimen S - a single crystal - in the action upon it of electromagnetic field, the source of action upon the specimen S of crystalline matter for solving its structure and determining its electron density distribution is a laser 13 mounted on the base 1, for its beam to be directed along the axis of rotation of the sample holder 9 (the Y-axis) by a mirror 14 supported on the bracket 11 through a removable extension bracket 15.

For studying single crystals in a magnetic field, the design of the corresponding configuration of the disclosed apparatus is basically similar, to the abovedescribed design. A difference, however, is that the source of action upon a sample of crystalline matter for solving its structure and determining its electron density distribution in magnetic action is in the form of an electromagnet 16 (FIG. 2) accommodating the investigated specimen S between its poles. In this embodiment the extended holder 9 passes

through the coil of one of the poles of the electromagnet 16, likewise supported on the bracket 11 through a removable extension bracket 15.

For investigating single crystals in an electric field, the electromagnet 16 is replaced by a capacitor (not shown). To conduct a study in physical action, the sample S can be placed into a high-pressure cell (not shown, either) with diamond anvils, likewise mounted on the holder 9, whereas to conduct a study in temperature conditioning, the bracket 15 is made to support a helium cryostat (not shown), or else an oven (not shown, either) for heating the sample S.

The disclosed apparatus for X-ray studies provides for conducting investigation with any combination of action upon a sample.

The embodiment of the apparatus for studying polycrystals in Bragg-Brentano focusing geometry, shown in FIG. 3, is basically similar to the apparatus illustrated schematically in Fig. 1. The difference in this case is that the sample holder 17 (FIG. 3) is so arranged that the plane of the sample S is perpendicular to the Y-axis. In this embodiment the X-radiation from the source 5 is preferably collimated with Soller slits (not shown), and the extension means 12 is of a variable length, e.g. telescopic.

The operation of the disclosed apparatus for X-ray studies of crystalline matter in its embodiments for investigating single crystals is, as follows.

When a single crystal is studied in the absence of external action, the sample S (FIG. 1) of a size smaller than 0.3 mm is arbitrarily glued to a glass or quartz holder 9 mounted on a standard goniometric head (not shown). By linear displacements in three perpendicular directions on the goniometric head, the centre of the sample S is matched with the point of intersection o f the geometric axis of rotation of the stage 2 and the geometric axis of rotation of the detector 6 and X-radiation source 5. The imminent angular measurements are taken from the axes of the orthogonal coordinate system whose centre is made to agree with the abovementioned point of intersection of the geometric axes. Thus, the Z-axis of the coordinate system is aligned with the geometric axis of rotation of the stage 2 and extends upward from the base 1, the Y-axis coincides with the geometric axis of rotation of the sample S by its rotation mechanism 10 and extends away from the mechanism 10, and the X-axis extends normally to the YZ plane, so that X, Y and Z define a right-hand vector triade. The coordinate system related to the system of axes of rotation in the disclosed apparatus for X-ray studies of crystalline matter is illustrated in more detail in FIG. 4 of the appended drawings where symbols universally employed for describing rotational angles in a four-circle diffractometer with equatorial geometry are used: phi (φ) - angle of rotation of the sample S about an axis parallel with the base 1; omega (ω) - angle of rotation of the source 5 of X-radiation about an axis parallel with the base 1; theta (θ) - angle of rotation of the detector 6 of diffracted X-rays about an axis parallel with the base 1, and chi (χ) - angle of rotation of the stage 2 about an axis perpendicular to the

base 1. Zero values of omega, chi and phi angles are chosen arbitrarily. In the presently described embodiment, the zero value of omega corresponds to a position where the source 5 of X-rays is aligned with the positive (+) branch of the Z-axis. Then the zero value of the Bragg angle theta corresponds to the alignment of the receiving slit of the X-radiation detector 6 with the negative branch (-) of the Z-axis, the zero value of chi corresponds to the mechanisms 8 (FIG. 1) and 7 for rotating the X-radiation source and detector being aligned with the positive (+) branch of the Y-axis (FIG. 4) by their own axes. The zero value of phi is chosen arbitrarily, but it should be maintained constant at least in the course of complete investigation of one specimen or sample. To measure reflection by the single crystal under study, the sample S stage 2, X-radiation source 5 and detector 6 of diffracted X-radiation are so set by operating the respective rotation mechanisms 10 (FIG. 1), 3, 7 and 8 and monitoring the readings of the corresponding angle-of-rotation transmitters (not shown) that the conditions of diffraction by a predetermined plane of the sample S should be satisfied. To determine the integral intensity of measured reflection, it is scanned by rotating the X-radiation source 5 (FIG. 4) and detector 6 with the sample S held immobile. A rotation of the source 5 and detector 6 in the same direction at the same angular speed corresponds to omega-scanning in a conventional four-circle diffractometer with equatorial geometry; omega/two-theta scanning is effected by rotating the source 5 and detector 6 at the same angular speed in opposing directions; and with the detector 6 held immobile and the source 5 rotated, the omega/theta scanning condition is satisfied. Any other

scanning mode is also attainable.

From the outcome of registration of all the reflections of the sample under study susceptible to measurement, the electron density distribution in the crystal is computed.

In the herein disclosed apparatus it is possible to study electron density distribution in weakly or poorly reflecting single crystals, by positioning the source 5 and detector 6 at a close spacing from the sample S under investigation.

When a single crystal has to be studied with an external action applied to it in a certain direction, e.g. the action of the laser 13 (FIG. 1), the single crystal under investigation is so oriented that the selected direction of the single crystal should align with the Y-axis, a mirror 14 1-2 mm in diameter is mounted on the bracket 15 and matched with the positive branch of the Y-axis, to throw the beam of the laser 13 upon the sample S. The rest of the investigation procedure is basically similar to the abovedescribed operation.

When a single crystal is to be investigated in a magnetic field, the electromagnet 16 (FIG. 2) having an axial bore through its core is mounted on the bracket 15 so that the axis of its magnetic flux should be aligned with the Y-axis, the sample holder 9 is passed through the axial bore, and the sample S is so attached that a selected direction of the crystal should align with the Y-axis. The rest of the procedure is similar to that described hereinabove.

The herein disclosed apparatus for X-ray studies of crystalline matter requires practically no readjustment for investigating polycrystals in Bragg-Brentano geometry. When a cylindrical sample is to be studied, it is set in the apparatus of the embodiment of FIG. 1 so that its axis should align

with the geometric axis of the rotation mechanism 10. A diffraction pattern is registered with chi equalling zero, and with the X-radiation source 5 and detector 6 being rotated at the same angular speed towards the positive branch of the X-axis.

To investigate a sample with a planar surface, the sample S is secured to the extremity of the extension means 12 (FIG. 3) perpendicularly to the Y-axis, its surface being matched to the Z-axis. By rotating the stage 2, chi is set at 90°, and by rotating the source 5 and detector 6 at the same angular speed towards the positive branch of the Y-axis a diffraction pattern of the polycrystalline sample S under study is registered. The diffraction pattern can be used for investigating the phase composition, measuring lattice periods, studying microdistortions. To study macrostrain in a sample, e.g. by the inclined diagram technique, inclined diagrams of diffraction reflections can be obtained by varying the value of chi, and measuring each time the selected diffraction line. In texture studies, registration of inverse pole figures is conducted by discrete variation of chi (by rotating the stage 2) and registration of a selected diffraction line with the source 5 and detector 6 held immobile, and phi being varied from 0° to 360°. The rest of studies of flat polycrystalline specimens can be conducted without any readjustment of the apparatus. The only condition to be satisfied is to ensure that the spacing between the sample S and the X-radiation source 5, on the one hand, and between the specimen S and the detector 6 of diffracted radiation, on the other hand, meet the focusing requirement of the Bragg-Brentano technique.

The herein disclosed apparatus for X-ray studies of crystalline matter allows for measuring the integral intensity of diffraction reflexes throughout the space about a single crystal without obscurations being imposed by the hardware of the apparatus, which allows for saving the investigation time otherwise spent on bypassing the obscured areas. The feasibility of making the mechanism for rotating the sample holder remote from the sample, brought about by the disclosed arrangement of the mechanisms of the apparatus and the incorporation of the extension means, provides for substantially reducing the "blind zone" created by the mechanism for rotating the sample holder, thus minimizing the influence of an interruption in data collection on the accuracy of electron density determination. Furthermore, the disclosed arrangement of the components of the apparatus provides for minimizing the spacing between the sample and the radiation source and detector, which allows for studying weakly or poorly reflecting crystals, as well as for investigating without major readjustments the structure, phase composition, texture, macro- and microdistortions of polycrystals.

CLAIMS

1. An apparatus for X-ray studies of crystalline matter, wherein a movable stage is mounted on a horizontal base and connected to a mechanism for its rotation about an axis perpendicular to the base; the stage carries a source of X-radiation and a detector of diffracted X-radiation reflected from a sample of crystalline matter, which are operatively connected to mechanisms for their independent relative and joint rotation about an axis parallel to the base; a holder of the sample of crystalline matter is operatively connected to a mechanism for its rotation about an axis parallel to the base, supported on the base with the aid of a bracket, wherein and the holder of the sample of crystalline matter, the mechanism for its rotation, bracket are disposed to one side of the axis of rotation of the stage.

2. An apparatus for X-ray studies as claimed in claim 1, wherein the holder of the sample of crystalline matter and the mechanism for its rotation about the axis parallel to the base are connected by an extension means.

3. An apparatus for X-ray studies as claimed in claims 1 or 2, comprising at least one source of action on the sample of crystalline matter for solving its structure and its electron density distribution during such action.

4. An apparatus substantially as set forth in any one of the preceding claims and as described herein above with reference to the accompanying drawings.

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